

Studies of the N K X-ray Emission Spectrum of Silicon Oxynitride

D. Fu, C.McGuinness, J.E.Downes, K.E.Smith (Boston U.) and G. Hughes (Dublin City U.)

Beamline: X1B

Introduction: Ultrathin films of silicon dioxide (SiO₂) and silicon oxynitride (SiO_xN_y) on silicon substrates are used widely in the semiconductor industry as gate dielectrics in transistors. Oxynitride films on silicon have superior device reliability, better resistance to dopant diffusion, alleviate interfacial strain and have a higher dielectric constant than pure oxide materials^[1]. Nitrogen is typically incorporated near the SiO₂/Si interface at concentrations of about 10¹⁵cm⁻². While there is a growing understanding of the process through which these oxynitride films are formed and their macroscopic dielectric and device properties there is still a lack of knowledge concerning the basic electronic structure of the nitrogen layer.

Methods and Materials: The SiO_xN_y films studied are those used by Intel as Process Of Reference (POR) samples in their manufacturing facilities worldwide. They consist of Si wafers coated with a 6Å layer of silicon oxynitride and capped with a 50Å layer of SiO₂. They have been studied by both x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES). The XAS spectra were obtained both by the sample drain current method and by total fluorescence yield methods while the XES spectra were recorded using a compact high-resolution grazing-incidence grating spectrometer. Prior to analysis the samples were etched in aqueous HF to remove the covering SiO₂ layer.

Results: A N 1s XAS spectrum was recorded from the SiO_xN_y POR sample with a resolution of 0.4eV and a N 1s XES spectrum was obtained with an outgoing photon energy resolution of 0.6eV. These spectra are shown in figure 1 below. The XAS and XES spectra are measures of the unoccupied and occupied partial density of states of the N 2p respectively. For comparison we show the published N 1s XES spectra of both α-Si₃N₄^[2] in figure 2 and molecular N₂^[3] in figure 3.

Conclusions: The recorded N 2p partial density of states show the similarity to both that of molecular nitrogen and that of α-Si₃N₄ (the two strongest peaks have an energy difference 2.01eV for SiON, 3.09eV for Si₃N₄ and 1.4eV for N₂). However band structure calculations of Si₂N₂O^[4] result in a more peaked N 2p partial density of states closer to the valence band maximum in broad agreement with that observed here. How N is bonded in SiON is still in debate.

Acknowledgments: This work has been supported in part by the DOE under grant number DE-FG02-98ER45680. G. Hughes wishes to thank the NSLS for partial funding. Our x-ray emission spectrometer is funded by the U.S. Army Res. Office under DAAH04950014.

References:

- [1] J.P. Chang et al., Journal of Applied Physics, **87**, 4449 (2000);
- [2] G. Wiech et al., Physical Review B, **49**, 5398 (1994);
- [3] P. Glans et al., Journal of Electron Spectroscopy and Related Phenomena, **82**, 193 (1996);
- [4] Y-N. Xu and W.Y. Ching, Physical Review B, **51**,17379 (1995).

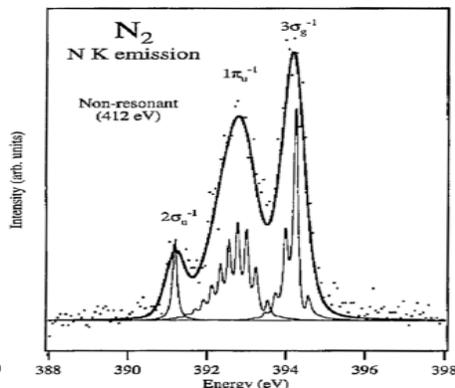
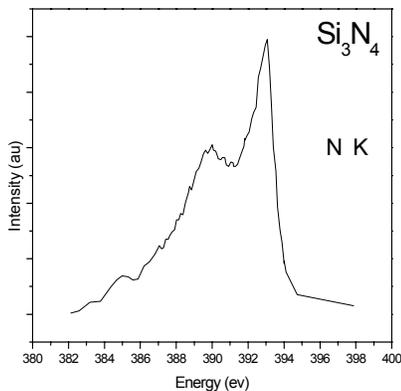
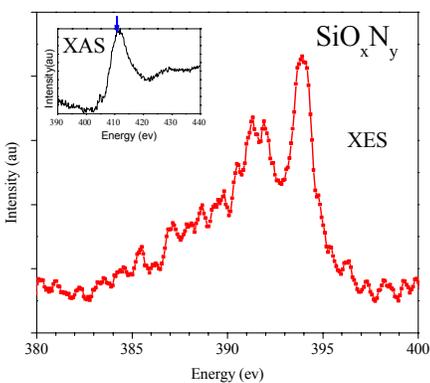


Figure 1: The recorded N 1s XES spectrum shown with the N 1s XAS spectrum (inset).

Figure (2) N K emission bands of α-Si₃N₄.^[2]

Figure (3) Non-resonant X-ray emission spectrum of N₂.^[3]